Identifying objective measures for Barossa Valley Shiraz grapes

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Chemical and spectral measures of grapes were previously applied to predict grape allocation grades for Cabernet Sauvignon, Shiraz and Chardonnay. Using the specific methods highlighted as being of importance to Shiraz grape quality in that study, a new project has continued efforts in this area, with the goal of understanding compositional aspects contributing to quality differences in Barossa Shiraz grapes and wines within the premium category.

INTRODUCTION

The identification and use of objective measures for the accurate determination of red grape quality remains a goal for many Australian grape and wine producers. Historically, grape colour was widely used as a quality measure, but this was later confounded by significant seasonal variation, as well as variability in sampling and analysis. Both the wine industry and the research community recognise the need for ongoing research into grape objective measures in order to appropriately reward growers, and for wineries to be able to stream fruit to specification. While many wineries perform routine analysis on grapes such as total soluble solids, pH and titratable acidity, there is a lack of know-how on how to apply and interpret newer analytical techniques. Ongoing collaboration between wine producers and researchers is essential to identify practical quality measures that are tailored to specific quality grades and wine styles.

BUILDING ON PREVIOUS KNOWLEDGE OF OBJECTIVE MEASURES FOR SHIRAZ GRAPE QUALITY

An earlier AWRI project aimed to identify the key objective measures in grapes which might be used to define commercial quality grading across a wide range of grades (Bindon *et al*. 2016, Bindon *et al*. 2017). This was particularly successful for Shiraz grapes, where the most important variables for defining quality grade were phenolics (colour and tannin) and nitrogen (amino acids and ammonia). Based on this successful proof of principle study, there was interest from another producer to use the same objective tools to understand the variation between different grades of Barossa Shiraz. This led to the initiation of a new project on Shiraz grape quality. The project looked more specifically at grape phenolics using new techniques such as extractable tannin and colour (Bindon *et al*. 2014), as well as non-targeted phenolic profiling (Lloyd *et al*. 2015), which enables multiple unknown compounds to be identified. Since total must nitrogen and individual amino acids are also known to influence the fermentation-derived volatile profile of wines (Vilanova *et al*. 2007), these measures were also highlighted as being of importance in the new project on Barossa Shiraz.

DESIGN OF A STUDY TO DEFINE SHIRAZ GRAPE QUALITY

In the 2017 vintage, the producer identified 20 Shiraz vineyards within the Barossa Valley that were within the premium 'intended use' classifications 1 and 2. Five samples were taken across each vineyard, and these were all completely destemmed and put through a series of analyses (Figure 1, see page 32). Since commercial winemaking could not be sufficiently controlled to determine potential impacts on wine outcomes, each grape batch was also put through a micro-fermentation (250g ferment) process in triplicate and analysed (Figure 1). Finally, for commercial winemaking, each vineyard was harvested and kept separate in the winery for fermentation and barrel ageing in old oak over 6-8 months. Commercial wines were then evaluated by a panel of winemakers (single samples evaluated during one tasting session) to assign an 'intended use' classification and were then analysed for their chemical and sensory properties at the AWRI. The assigned 'intended use' grades spanned four quality categories: 1 (highest quality), 1.5, 2 and 3. Data generated from the study were analysed using multivariate statistical techniques in order to predict the respective grape and wine grades.

AT A GLANCE

- Building on previous work on grape objective methods multivariate techniques were applied to understand the variation between different grades of Barossa Shiraz
- For this data set grape quality grades could not be defined by grape objective measures alone
- Certain high quality vineyards did not produce wines in the expected quality category
- Higher levels of grape amino acids and ammonia were associated with lower wine quality
- Lower grape colour was associated with lower wine quality
- Higher grade wines were less brown and more purple than lower grades, and had an absence of off-odours
- Results suggest that grape nitrogen should be monitored in the vineyard and at the winery to optimise wine quality.

TOWARD THE IDENTIFICATION OF CHEMICAL MEASURES TO PREDICT GRAPE QUALITY GRADES

Using the results of grape analysis alone, it was not possible to accurately predict the 'intended use' grade of more than 47% of the grape samples using multivariate statistics. Nevertheless, some grape-based measurements could be identified as more significant than others in distinguishing grape grades 1 and 2. Prediction models were also built using data from the micro-ferment wines associated with each grape batch. The wines were assessed immediately at the completion of fermentation, and were therefore not aged, and reflect only the basic extraction and conversion of compounds during fermentation. The inclusion of the wine data gave stronger models for grape grade prediction using multivariate statistics, at 70% accuracy. This enabled the identification of both grape and wine variables that were relevant in defining the two fruit grades (1 and 2). In terms of grape phenolics, total and extractable tannin were lower in grade 1 fruit than grade 2 fruit. Conversely, extractable (but not total) grape anthocyanin was higher in grade 1 fruit, and this was correlated with higher wine colour density and anthocyanin in the micro-ferment wines, also significant variables in the prediction model. Despite the finding that tannin and colour were important in the prediction of grape grade, using the UV-visible spectrum of either grapes or wine alone did not produce successful prediction models, in contrast to the results of a previous study (Bindon *et al*. 2016, Bindon *et al*. 2017). On the other hand, when data from non-targeted grape and wine phenolic analysis was added to the prediction models the accuracy was improved up to 79%, and a further 19 non-identified wine compounds and three non-identified grape compounds were shown to be significant in defining the grape quality grades. These compounds will be further investigated and identified by Metabolomics Australia.

Grape nitrogen and wine fermentation products were also assessed for their importance in defining grape quality grade. It was found from the prediction models that ethyl acetate, butanoic acid and a number of fermentation esters associated with 'berry' aromas (Pineau *et al*. 2009) were lower in wine made from grade 1 fruit. Furthermore, grade 1 grapes had higher concentrations of yeast assimilable nitrogen (YAN), ammonia and certain amino acids than grade 2 grapes.

The results of the grape grade study showed that although some grape-based measures could be identified as relevant in the prediction of grape grade, strong models of prediction could not be developed without the inclusion of wine data. This indicates that the conversion of grape metabolites during fermentation is related to, but not strictly correlated with, their concentration in or extractability from the grape source. Further research to identify important wine metabolites from the non-targeted phenolic analysis may potentially shed light on other relevant compounds not detected in the grape-based assays but that may be important in the definition of quality grade in the premium category.

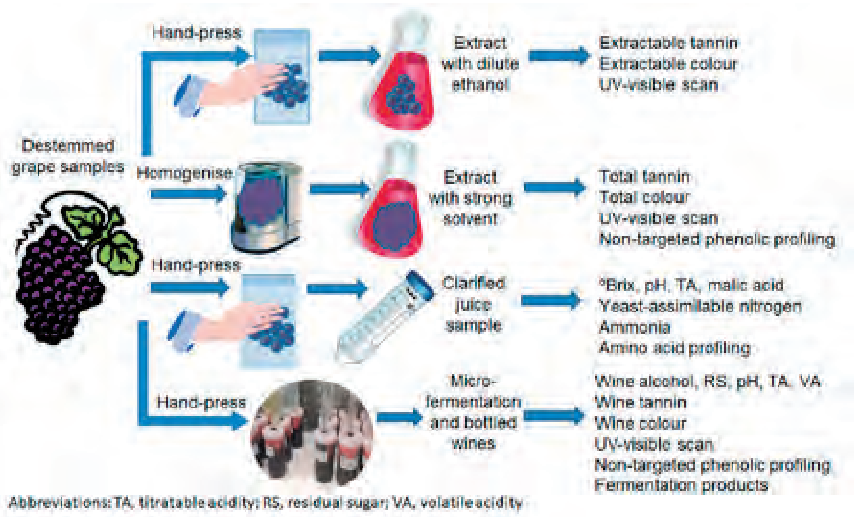

Figure 1. Procedure followed to obtain chemical measurements from grapes and wines in order to predict grade.

DEFINING WHY GRAPES FROM SOME PREMIUM VINEYARDS DO NOT ALWAYS PRODUCE PREMIUM WINE

Although the vineyards selected for the study were only of premium grape grades 1 and 2, it was evident after the commercial winemaking was completed that the vineyard grading system did not closely reflect the final wine grade assigned by the winemaker panel. Proportionally, 46% and 57% of grape grades 1 or 2 respectively produced wines that were graded 1 or 1.5. The remaining 53% and 43% of the vineyards graded at 1 and 2 therefore produced wines that were graded 2 or 3, respectively. In light of this finding, it was deemed relevant to the goals of the project to determine whether grape or wine chemical measures might be useful in predicting the 'intended use' wine grade, since this was of commercial importance. The same grape and wine chemical data used in the prediction of grape grade was therefore applied in models to predict the final wine grade. From this process, it was found that wine grades 1, 1.5 and 2 could not be distinguished by the chemical data, but the models could strongly predict wine grade 3, at between 71 and 75% accuracy, depending on the type of data used.

Using the combined grape and micro-ferment wine data, it was found that grape batches that produced grade 3 wines had higher levels of grape nitrogen, including ammonia and total amino acids, including total YAN and proline (Figure 2). This finding was in contrast to results from the prediction of grape grade, where YAN and ammonia were elevated in grade 1 grapes relative to grade 2. YAN averages across wine grade categories were ~150mg/L for grapes that produced wine grades 1 and 1.5, increasing to ~260mg/L and ~380mg/L for grade categories 2 and 3, respectively. A strong negative correlation with nitrogen measures was found for certain important fermentation products in micro-ferment wines (Figure 2), including ethyl 2-methylpropanoate ('blackberry'), 2-methylbutyl acetate ('banana'), 2 phenyl ethyl ethanol

('fruity'/'floral'/'rose') and 2-methylbutanol ('roasted'), all of which were lower for grade 3. On the other hand, wine volatile acidity, including acetic acid and propanoic acid ('pungent'/'rancid') were higher in micro-ferment wines associated with the grade 3 category, and these measures were all correlated with higher nitrogen in the grape source.

The sensory properties of the commercial wines from the different grade classes were also compared and it was found that the negative aroma attributes 'drain' and 'cooked vegetable' were rated higher in the grade 3 category than the higher grades (Figure 3, see page 34). Small losses in 'dark fruit' aroma and flavour were also seen for grade 3 wines, accompanied by increases in 'red fruit' aroma and flavour. Models developed to predict wine sensory properties showed that grape nitrogen measures, including many amino acids, strongly predicted the aromas and flavours associated with the grade 3 category. It is therefore likely that an excess of fermentable nitrogen in grade 3 grapes was associated with a loss of important yeast-derived volatile compounds, and the formation of higher levels of negative compounds such as acetic acid and propanoic acid. Excess fermentable nitrogen may also have led to issues with the formation of hydrogen sulfide, or other undesirable 'stinky' volatile sulfur compounds, which may have contributed to the perceived negative sensory attributes (Ugliano *et al*. 2010), but were not measured in the study. Nevertheless, the results present a convincing case that higher levels of grape nitrogen may have contributed to lower wine quality following the commercial fermentation process, which led to wine produced from otherwise high quality grape parcels being assigned to a lower category.

Grape phenolics were not found to predict the grade 3 category as strongly as grape nitrogen measures. Nevertheless, grapes that produced grade 3 wines had lower total and extractable grape colour. In terms of the visual perception of the Shiraz wines (Figure 3B), it was found that the panel's ratings for opacity and purple colour were far lower in grade 2 and 3 wines than in grades 1 and 1.5. These differences were accompanied by increased perception of brown colour as wine quality decreased. In looking at the chemical attributes that defined colour in the micro-ferment wines, total wine colour did not change significantly among the different wine grades. Rather, grade 3 micro-ferment wines had a browner hue and a higher chemical age (proportionally more pigments were resistant to bisulfite early in the life of the wine). These results suggest that the grade 3 commercial wines may have prematurely developed an aged character. Sensorially, the grade 2 and 3 wines were also defined by somewhat lower astringency than the higher wine grade categories (Figure 3B). Interestingly, this was not strongly related to the tannin concentration in the commercial wines themselves, since oenological tannins were added as standard winemaking practice. However, in comparing the wine tannin from the micro-ferments with final commercial wine astringency (Figure 4), it was evident that grape-derived tannin was differentiated between lower (2 and 3) and higher (1 and 1.5) grades, and tracked with changes in astringency. This suggests that grape-derived tannin may be more relevant in determining the astringency of a wine than added tannin.

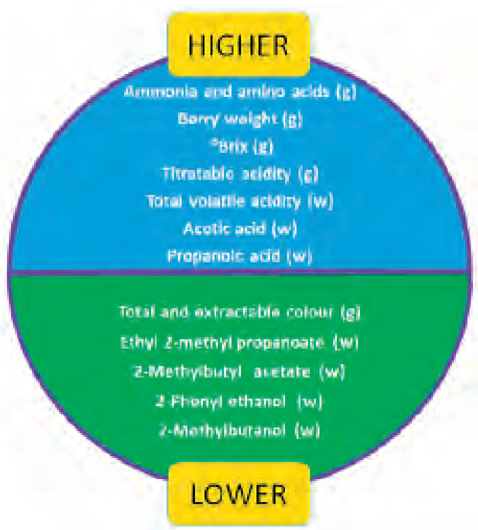

Figure 2. Characteristics of grapes (g) and micro-ferment wines (w) that were associated with an 'intended use' wine grade 3.

THE NEXT STEP: THE IMPORTANCE OF MONITORING BASIC GRAPE CHEMISTRY IN THE VINEYARD

The results of the first (2017) season of the study highlighted some important new knowledge related to both grape and wine quality. Grape colour is well known to be related to wine quality, and this was again confirmed for both grape grade and wine grade. However, grape nitrogen has not previously been attributed the same importance as colour, and is not often used as a standard measure of 'fitness for purpose' when processing grapes at the winery. The data from this study suggested that vineyards otherwise identified as being

of premium grade but with high grape nitrogen could potentially lose quality during the winemaking process, possibly due to the formation of off-odours or reduced levels of key positive aroma compounds. Measurement of nitrogen in the vineyard through petiole or juice analysis is currently performed by only 40% or less of Australia's producers (Nordestgaard 2019). Approximately 65% of wineries that crush more than 10,000 tonnes add diammonium phosphate (DAP) to must based on YAN measurements, but this drops to 30% or less for smaller producers at 1000 tonnes or under (Nordestgaard 2019). In light of this, the measurement of grape juice YAN prior to DAP additions in the winery is relatively simple and accessible for many wineries and can be used to prevent excess addition of nitrogen in must. In consideration of the results presented in this article, increasing the use of nitrogen measurements in both small- and larger-scale wineries within Australia could be an important first step to ensure the maintenance and improvement of Shiraz wine quality.

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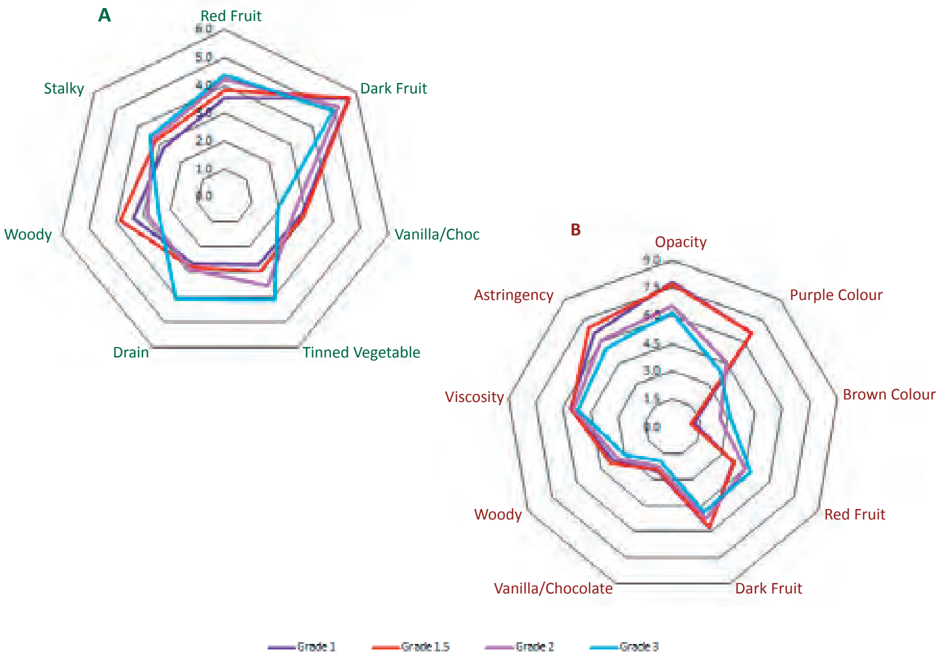

Figure 3. Significantly different sensory attributes for commercial Shiraz wines grouped for grades 1 to 3 from a single producer showing A. aroma attributes and B. visual and palate attributes.

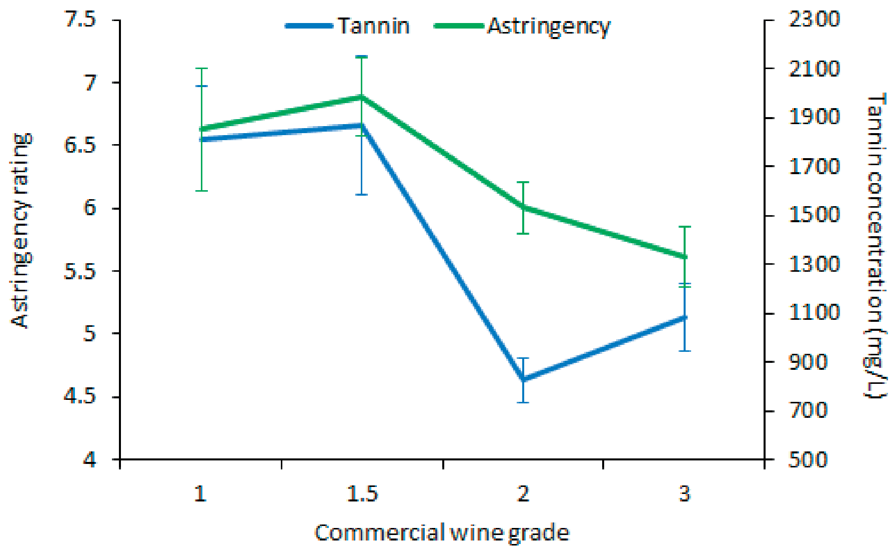

Figure 4. Tannin concentration in micro-ferment wines made from batches of Shiraz grapes for which final commercial grade classifications were 1, 1.5, 2 and 3, showing the associated astringency rating for each category (data shown as mean and standard deviation).

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